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(71) Applicant (*for all designated States except US*): EVEREADY BATTERY COMPANY, INC. [US/US]; 25225 Detroit Road, Westlake, OH 44145 (US).

(71)(72) Applicant and Inventor: URRY, Lewis, F. [US/US]; 36263 Butternut Ridge Road, Elyria, OH 44039 (US).

(74) Agents: WELSH, Robert, W. et al.; Eveready Battery Company, Inc., 25225 Detroit Road, Westlake, OH 44145 (US).

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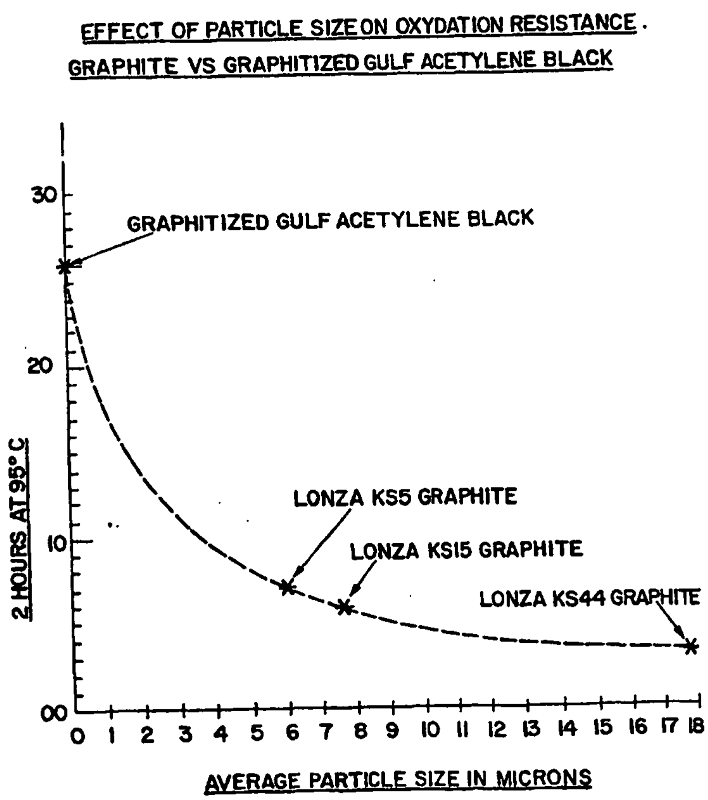
(54) Title: HEAT TREATED FINE CARBON FOR ALKALINE MANGANESE CATHODES

(57) Abstract

Heat treated fine carbon has small particle size and can be used as the electroconductive element in cathodes of electrochemical cells to reduce the volume taken up by non–active materials by increasing contact between the active material and the electroconductive element.



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HEAT TREATED FINE CARBON FOR ALKALINE MANGANESE CATHODES

BACKGROUND OF THE INVENTION

The present invention generally relates to a heat treated fine carbon as a conductor in a cathode mixture of electrochemical cells.

Conventionally, the positive electrode of alkaline manganese batteries comprises mixtures of electrolytic manganese dioxide (EMD) as the positive electrode active material, and carbon as the electroconductive material. The electroconductive material is necessary because the specific conductivity of manganese dioxide alone is extremely low. When electroconductive carbon materials are used in large quantities, the quantity of manganese dioxide that can be used in a battery's fixed internal volume is decreased. Consequently, the discharge capacity density of the battery is decreased to a very great extent. On the other hand, when an insufficient amount of the electroconductive carbon is used, there is decreased contact between the manganese dioxide and the carbon. This results in a decreased electron conduction network, and the overall utilization rate of the manganese dioxide in the electrode is thereby decreased. By using a finer conductor material, especially compared to the size of the manganese dioxide, a lesser amount of conductor material is needed to get an adequate electron matrix. The finer particle-size particles reduce the volume percent solids without reducing the input per volume of active materials, or increases the input of active materials per unit volume of the solids packing. The advantages of using a very fine conductor material are well known, but difficult to achieve.

Graphite has been widely used as a conductor and has the advantage of being highly oxidation resistant. However, due to graphite's particle size (the smallest particle size commercially available is about 2.5 microns), a large volume percent of the graphite conductor is necessary to provide electron distribution to the active material throughout discharge. One approach to reducing the minimum volume percent of the graphite conductor is to grind it finer; however, this is difficult to do and costly. Moreover, the finest ground material commercially available is still not less than 0.5 micron.

Acetylene black, the finest of the carbon blacks, has also been used as a conductor, and has the advantage of finer particle size. However, conventional acetylene black is oxidized much faster by $Mn0_2$ than graphite, and thus, storageability suffers as MnO_2 capacity decreases and carbonate is produced. Optimization of the mixing ratios cells using conventional acetylene black and manganese dioxide for high efficiency is taught by U.S. Patent No. 5,017,445. This reference teaches using an acetylene black of a limited specific surface area, with the weight ratio of manganese dioxide:acetylene black ranging from 7:1 to 12:1.

It is desirable to have a fine carbon conductor that has the optimum properties good oxidation resistance and permits good electrochemical performance at a very low volume percent (<6%) of the positive electrode.

SUMMARY OF THE INVENTION

This invention is an electrochemical cell having an anode, a cathode, and an electrolyte, wherein the cathode comprises a heat-treated fine carbon as an electronic conductor.

In yet another aspect, this invention is an alkaline cell having a cathode comprising a conductor at less than 6 volume percent of the positive electrode.

In still another aspect, this invention is an alkaline cell having a cathode mixture comprising fine carbon having a high oxidation resistance of less than 30 milliliters $K_2Cr_2O_7$/gram, as determined by a potassium dichromate digestion test described herein.

The alkaline cell of this invention has a cathode that has good oxidation resistance, and good electrochemical performance at a low volume percent of the positive electrode.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph of effect of particle size on oxidation resistance of heat treated fine carbon vs. graphites.

Figure 2 is a graph comparing three D-size cells containing different types of conductor materials.

DESCRIPTION OF THE INVENTION

According to the present invention, a mixture comprising a heat treated fine carbon with manganese dioxide provides an improved positive electrode for alkaline cells. The heat treated fine carbon of this invention can be produced using a fine carbon material such as acetylene black, that is treated, for example, at a temperature

of about 3000 °C in an inert atmosphere for about one hour. The resulting heat treated fine carbon particles have an average particle size diameter in the range of about 50 Angstroms to about one micron, as measured by scanning electron microscopy. The fine carbon particles facilitate formation of an electronically conductive network, with a lesser volume percent of the conductor as compared to graphite, thereby resulting in enhanced utilization of the manganese dioxide particles on the overall mixed positive electrode active material.

The fine carbon, as used in this invention, can be obtained from various commercial sources such as Chevron Corporation, Cabot Corporation, Denka Corporation, Sedema Corporation, to name a few. After subjecting the fine carbon to heat treatment, the carbon particles have improved oxidation resistance over conventional fine carbon, as measured by the following potassium dichromate test.

> A gram of the material to be evaluated is accurately weighed in a 100 milliliter volumetric flask. A mixture of 75 ml 0. 1 N $K_2Cr_2O_7$ solution and 15 ml of 1:1 H_2SO_4 is added to the flask. The flask is sealed with a stopper and transferred to a water bath, maintained at 95 °C for 4 hours. The flask is removed from the water bath and cooled on ice. A 1:1 solution of H_2SO_4 is made, and 10 milliliters of the H_2SO_4 solution are added to the flask, and mixed thoroughly. A portion of the solution is centrifuged. An aliquot of the centrifuged clear solution is titrated with 0.1 N ferrous ammonium sulfate using sodium diphenylamine sulfonate as
>
> indicator. A solution blank is run along with the samples. The normality factor is calculated from the blank which converts milliliters

Fe^{++} to milliliters $Cr_2O_7^{-2}$. The normality factor is used to calculate the number of milliliters of potassium dichromate solution consumed per gram of sample in a given time.

The oxidation resistance is expressed as the number of milliliters of $K_2Cr_2O_7$ solution consumed per gram of sample. The lower the value, the greater its resistance to oxidation. The heat treated fine carbon according to this invention is 4.5 times more resistant to oxidation compared to the starting material.

RESISTANCE TO OXIDATION

Carbon Material	Oxidation resistance (milliliters of $K_2Cr_2O_7$ consumed per gram of sample)
Chevron Acetylene Black - conventional	118.3 mL/gram
Chevron Acetylene Black - heat treated	25.83 mL/gram

DETAILED DESCRIPTION OF DRAWINGS

Figure 1 is a graph of effect of particle size on oxidation resistance of heat treated fine carbon vs. graphites. As can be seen by this graph, the carbon after graphitization had the same oxidation resistance as graphite per unit surface area or particle size.

Figure 2 is a graph comparing three D-size cells containing different types of conductor materials. Cell 1 has heat treated acetylene black as a conductor at 5.8 volume percent; cell 2 has graphite as a conductor at 13.7 volume percent; and cell 3 has combined graphite and conventional acetylene black.

EXAMPLES

Three D-size alkaline cells are constructed for comparison.

A first cell is constructed using an acetylene black in the cathode mixture. The acetylene black, obtained from Chevron Corporation, is subjected to heating at 3000°C for one hour in an inert atmosphere. The resulting heat treated acetylene black particles, having average diameter of about 75 Angstroms, is mixed with electrolytic manganese dioxide active material and teflon as a binder, in the relative volume ratios of 7.7 volume percent carbon, 90.9 volume percent of electrolytic manganese dioxide, 1.4 volume percent teflon. The mixture is then packed to a solids packing of 75 volume percent, so that in the finished cathode, carbon is present at 5.8 volume percent, electrolytic manganese dioxide is 68.2 volume percent, teflon is 1.0 volume percent, with the remainder being non-solids, mainly as electrolyte and void volume.

A second comparative cell is constructed using a cathode comprising 12 volume percent graphite, 62 volume percent electrolytic manganese dioxide, and 1 volume percent teflon as binder.

A third comparative cell is constructed using a cathode comprising 14 volume percent combined graphite and conventional acetylene black, 54 volume percent electrolytic manganese dioxide, 7 volume percent inorganic binder.

Thus, all three cells were constructed with the cathode having a total 75 volume percent solids. The remaining 25 volume percent represents non-solids electrolyte filling at cell assembly. The three cells were subjected to a 2.3 ohm continuous discharge. The results, as can also be seen in Figure 3, show that the cell comprising the heat treated acetylene black exhibited a much higher discharge voltage profile than cells with conventional acetylene black cathode mixture.

Although the present invention has been fully described by way of example with reference to the accompanying drawings, it is to be noted here that various changes and modifications will be apparent to those skilled in the art. Therefore, unless otherwise such changes and modifications depart from the scope of the present invention, they should be construed as being included therein.

CLAIMS:

1. An electrochemical cell having an anode, a cathode, and an electrolyte, said cathode comprising a heat treated fine carbon.

2. An electrochemical cell having an anode, a cathode, and an electrolyte, said cathode comprising less than 6 volume percent of a conductor present in the cathode.

3. The electrochemical cell according to claim 1, wherein the fine carbon is acetylene black.

4. The electrochemical cell according to claim 1, wherein the fine carbon has an average particle diameter from about 50 Angstroms to about 1 micron.

5. The electrochemical cell of claim 1, wherein the fine carbon has an average particle diameter between about 50 Angstroms to about 200 Angstroms.

6. The electrochemical cell according to claim 1, wherein the fine carbon has an oxidation resistance of less than 30 milliliters 0.1 N potassium dichromate digested per gram of carbon, as measured by a potassium dichromate test.

7. The electrochemical cell according to claim 1, wherein the electrolyte is potassium hydroxide.

8. An electrochemical cell having an anode, a cathode, and an electrolyte, said cathode comprising a heat treated fine carbon having an oxidation resistance of less than 30 milliliters 0.1 N potassium dichromate digested per gram of carbon, as measured by a potossium dichromate test.

9. The electrochemical cell according to claim 2, wherein the fine carbon is acetylene black.

10. The electrochemical cell according to claim 2, wherein the average particle diameter of the heat treated carbon is from about 50 Angstroms to about 1 micron.

11. The electrochemical cell of claim 2, wherein the conductor has an average particle size between about 50 Angstroms to about 200 Angstroms.

12. The electrochemical cell according to claim 2, wherein the conductor has an oxidation resistance of less than 30 milliliters 0.1 N potassium dichromate digested per gram of carbon, as measured by a potassium dichromate test.

13. An electrochemical cell having an anode, a cathode, and an electrolyte, said cathode comprising a conductor having an oxidation resistance of less than 30 milliliters 0.1 N potassium dichromate digested per gram of carbon, as measured by a potassium dichromate test.

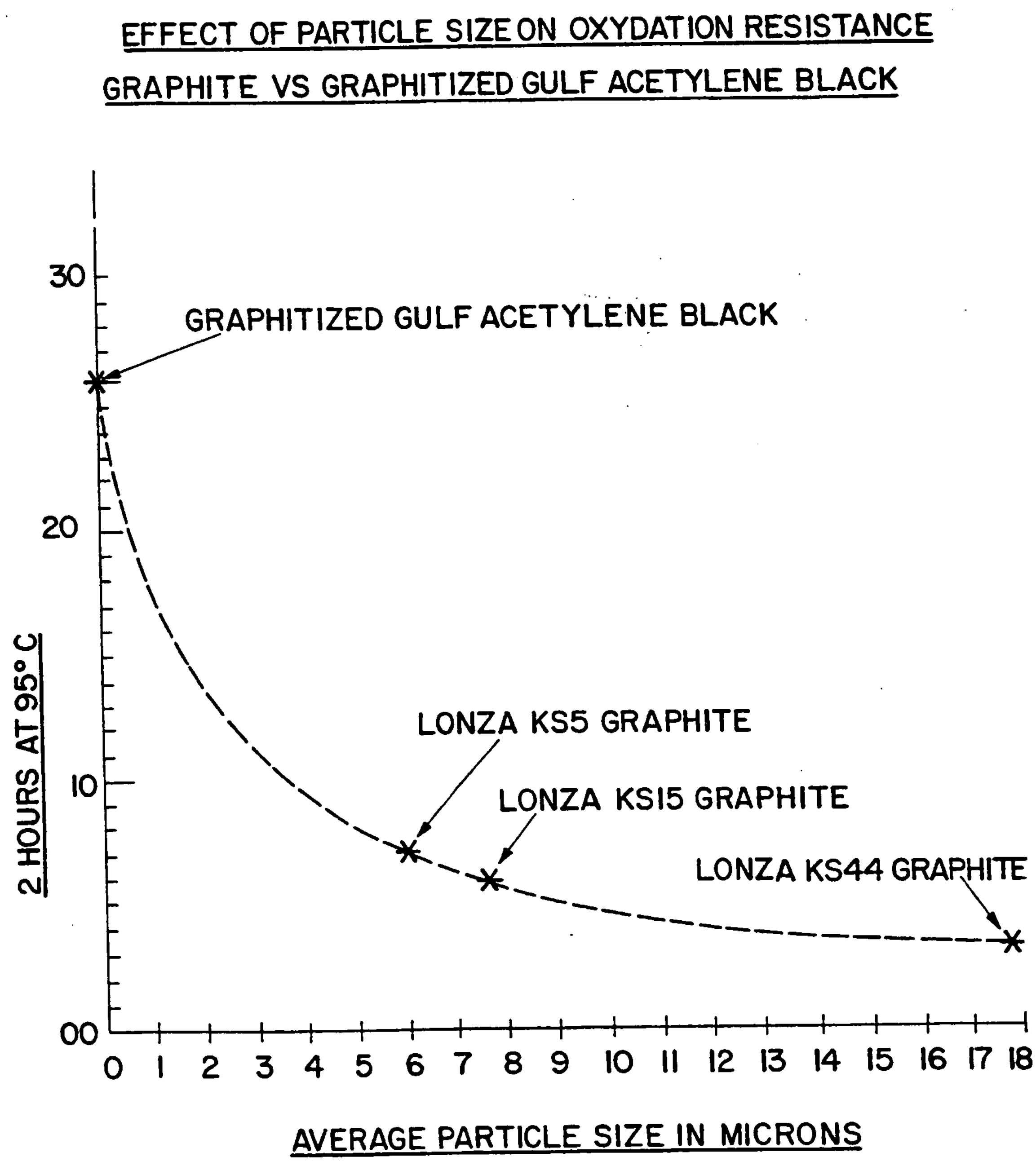
EFFECT OF PARTICLE SIZE ON OXYDATION RESISTANCE
GRAPHITE VS GRAPHITIZED GULF ACETYLENE BLACK
30
20
10
00
2 HOURS AT 95° C
GRAPHITIZED GULF ACETYLENE BLACK
LONZA KS5 GRAPHITE
LONZA KS15 GRAPHITE
LONZA KS44 GRAPHITE
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
AVERAGE PARTICLE SIZE IN MICRONS

Fig. 1

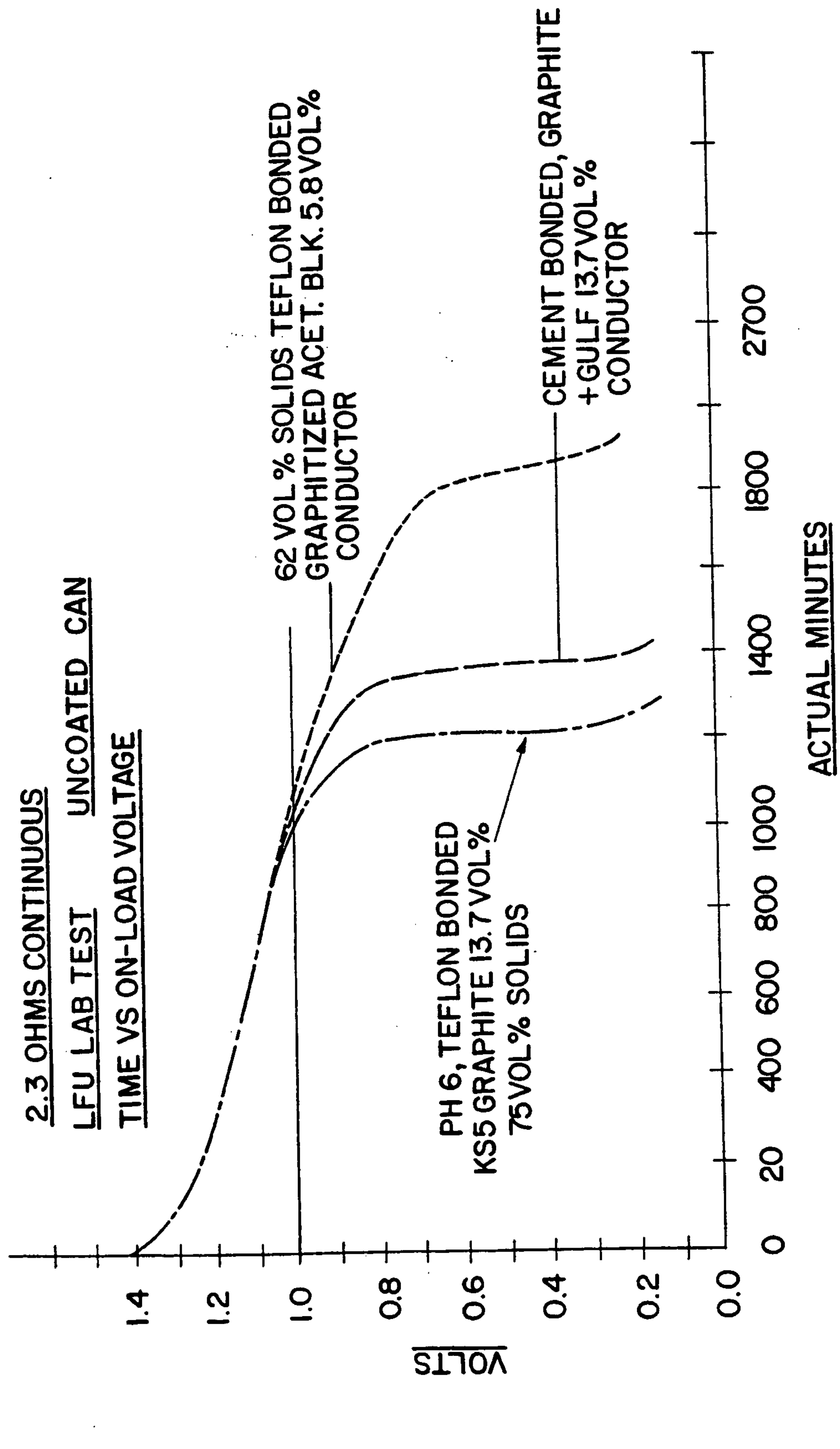
2.3 OHMS CONTINUOUS
LFU LAB TEST
UNCOATED CAN
TIME VS ON-LOAD VOLTAGE
62 VOL % SOLIDS TEFLON BONDED
GRAPHITIZED ACET. BLK. 5.8 VOL%
CONDUCTOR
CEMENT BONDED, GRAPHITE
+GULF 13.7 VOL %
CONDUCTOR
PH 6, TEFLON BONDED
KS5 GRAPHITE 13.7 VOL%
75 VOL% SOLIDS
VOLTS
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
20
400
600
800
1000
1400
1800
2700
ACTUAL MINUTES

Fig. 2

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/08825

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 H01M4/62 H01M4/50

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 014, no. 222 (E-0926), 10 May 1990 & JP 02 056857 A (MATSUSHITA ELECTRIC IND CO LTD), 26 February 1990 see abstract	1,2,4,5, 10,11
A		13

X	CHEMICAL ABSTRACTS, vol. 104, no. 12, 24 March 1986 Columbus, Ohio, US; abstract no. 92092y, NISHII, TOSHIBUMI: "New-grade carbon black" XP002073759 see abstract & JP 60 152 569 A (MITSUBISHI)	1

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[X] Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search	Date of mailing of the international search report
5 August 1998	18/08/1998

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INTERNATIONAL SEARCH REPORT

International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	STOECKLI H F ET AL: "ON THE PHYSICO-CHEMICAL PROPERTIES OF CARBON BLACKS IN RELATION TO THE PERFORMANCE OF ZN/MNO2 BATTERIES" PROGRESS IN BATTERIES & BATTERY MATERIALS, vol. 15, 1996, pages 81-87, XP000727411 see experimental ---	1
A	EP 0 322 806 A (MATSUSHITA ELECTRIC IND CO LTD) 5 July 1989 see claim 1	3,9
A	& US 5 017 445 A (ASHIHARA R.) cited in the application -----	

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 98/08825

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		US 5017445 A	21-05-1991

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